

Resonant inelastic x-ray scattering in amorphous carbon nitride.

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INTRODUCTION

Even though amorphous carbon nitride has been the subject of an enormous research effort in the last decade, its local structure is largely unknown at the atomic scale, the many types of possible nitrogen configurations being the main problem. Core level spectroscopic techniques offer a great hope of solving this question, but the interpretation of these spectra is challenging. In the present paper, we study a type of amorphous carbon nitride for which the various N 1s components cannot be resolved in the photoemission and absorption spectra. This lack of detail in the core level spectra is due to the highly disordered structure of this material. We will use the high selectivity of resonant x-ray fluorescence spectroscopy to resolve and identify the various types of nitrogen in reactively sputtered amorphous carbon nitride.

EXPERIMENTAL DETAILS

The samples were prepared by reactive DC sputtering of graphite in a nitrogen plasma. A 50 micron wide copper tube discharged a jet of nitrogen gas at 2 atm pressure (inside the tube) into an ultra high vacuum chamber attached to a photoemission spectrometer. The capillary was placed at a 3 mm distance from a graphite target polarized at 5 kV. The sample was grounded and placed in front of the target at a distance of 10 mm. The plasma current was 1 mA. A bright blue glow was confined in the small region between the capillary and the target. The x-ray fluorescence measurements were made at the Rowland circle x-ray emission spectrometer at beamline 8.0 of the Advanced Light Source. The x-ray emission energy resolution was 0.4 eV and the excitation energy resolution was 0.2 eV.

RESULTS AND DISCUSSION

The set of N 1s emission spectra as a function of excitation and emission photon energies is shown in Fig. 1. The elastic peak is clearly apparent from 397 to 407 eV excitation energy. The features around 399 eV excitation energy are π^* resonances, while those around 407 eV are σ^* resonances. For of the π^* resonance there are two emission maxima at 394.8 and 392.4 eV while at other excitation energies only the maximum at 394.8 eV remains. All emission peaks remain nearly fixed as the excitation energy is scanned. This is interesting because in the x-ray emission spectra of ordered solids such as graphite and diamond a strong dependence of the emission energies on excitation energy has been found.¹ This is due to an electron-hole correlation effect first described by Ma *et al.*² As the momentum contribution of the x-ray photons is negligible compared to that of the electrons, the inelastic scattering process can be treated as a vertical excitation for which the crystalline momentum of the excited electron is the same as that of the valence band hole. As the photon energy is scanned, the k vector of the excited electron changes according to the dispersion of the conduction band. The probability of decay to the core hole is higher for valence band electrons with the same k vector as the excited conduction band electron

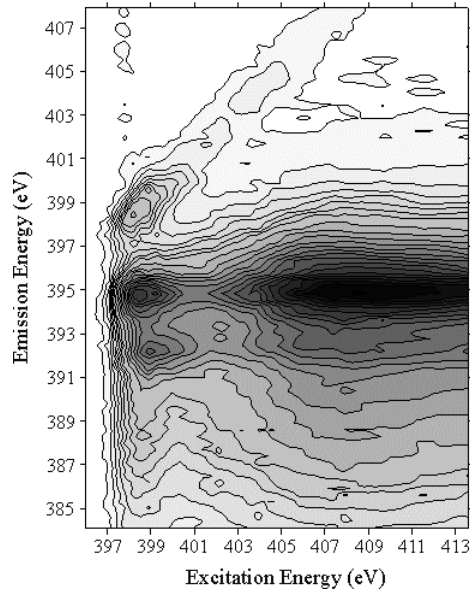


Fig. 1. X-ray emission intensity as a function of excitation energy and emission energy in the N 1s threshold region.

(this is the electron-hole correlation effect). Therefore, the energy loss in the x-ray inelastic scattering process is determined by the gap between the conduction and the valence band at the point in k space determined by the excitation energy and the conduction band dispersion. In some highly disordered solids, in insulators, and in atomic systems, the electron-hole pair is not delocalized and therefore it does not have a well-defined k vector (this is simply a consequence of the Heisenberg uncertainty principle). In this case, the correlation between the excited electron and the valence band hole should be expected in real space rather than in reciprocal space. This explains why the x-ray emission spectra of carbon nitride do not show dispersion with the excitation energy. There is no electron-hole correlation in k space because the k vector of the excited electrons is not well defined.

We have fitted all x-ray emission spectra using a set of gaussian curves with fixed width and position. For simplicity we have used the minimum number of Gaussian curves that yield a reasonable fit to the emission spectra at all excitation energies. Only the intensities are photon dependent and the parameters defining the gaussian peaks (emission energy and width) have been optimized using the least square method for all emission spectra simultaneously. The emission energies and widths are summarized in the following table

Emission Peak	Emission Energy (eV)	Width (eV)
E_1	390.2	4.0
E_2	392.4	0.8
E_3	394.8	0.7
E_4	395.6	1.6

The dependence of the emission peak intensities on excitation energy can be interpreted as an x-ray absorption spectra (XAS) in the partial fluorescence yield (PFY) mode and these are shown in Figure 2. The lineshape of these PFY curves provides information on the meaning of the

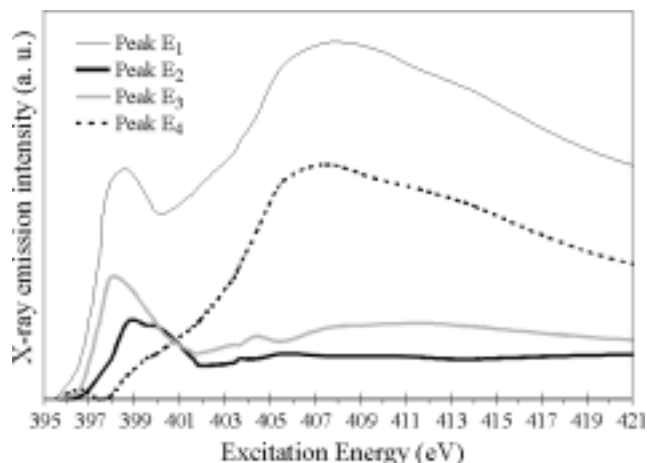


Fig. 2. Partial Yield Fluorescence spectra corresponding to the four x-ray emission peaks defined above.

corresponding x-ray emission peaks. The π^* resonance in the PFY curve corresponding to emission peak E_2 (392.4 eV emission energy) is centered around 399.5 eV. In previous studies³ it has been found that the π^* x-ray absorption resonance due to CN triple bonds appears at 399.5 eV. Furthermore, it is known that this type of nitrogen has a very weak σ^* resonance, and the PFY curve corresponding to E_2 almost has no σ^* resonance at all. Therefore it seems reasonable to assign emission peak E_2 to nitrogen with one carbon neighbor. The PFY curve corresponding to emission peak E_3 (394.8 eV) has a weak σ^* resonance at energies between 407 and 413 eV, in the range expected for nitrogen double bonds. The π^* resonance is at 398.2 eV, this π^* resonance energy being characteristic of nitrogen with two carbon neighbors³. The PFY curve corresponding to emission peak E_4 (395.6 eV emission energy) shows almost no π^* resonance, so this emission peak probably corresponds to nitrogen single bonds. Peak E_1 seems to be merely the high energy loss tail of the spectrum as the corresponding PFY curve has the same overall shape as the total fluorescence yield NEXAFS spectrum, so it does not seem to be associated to a particular type of nitrogen environment.

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REFERENCES

- ¹J.A. Carlisle, *et al.*, Phys. Rev. Lett. **74**, 1234 (1995).
- ²Y. Ma, *et al.*, Phys. Rev. Lett. **69**, 2598 (1992).
- ³J.M. Ripalda, *et al.*, Phys. Rev. B. **60**, R3705 (1999).

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